

# Labile Rhodium(I)–N-Heterocyclic Carbene Complexes

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**ABSTRACT:** Neutral square-planar complexes  $\text{Rh}(\text{acac})(\text{IPr})(\eta^2\text{-olefin})$  have been prepared from  $[\text{Rh}(\mu\text{-Cl})(\text{IPr})(\eta^2\text{-olefin})]_2$  (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene; olefin = cyclooctene, ethylene) and sodium acetylacetonate (acac). Protonation of the acetylacetonato complexes with triflic acid open the way to the formation of the putative bare  $[\text{Rh-IPr}]^+$  fragment that has been stabilized at low temperature by labile ligands such as triflate, cyclooctene or acetonitrile to generate  $\text{Rh}(\text{OTf})(\text{IPr})(\eta^2\text{-coe})$ ,  $[\text{Rh}(\text{IPr})(\eta^2\text{-coe})(\text{NCCH}_3)_2]\text{OTf}$  and  $[\text{Rh}(\text{IPr})(\text{NCCH}_3)_3]\text{OTf}$  complexes. Derivative  $[\text{Rh}(\text{IPr})(\eta^2\text{-coe})(\text{NCCH}_3)_2]\text{OTf}$  was further characterized by an X-ray diffraction analysis.

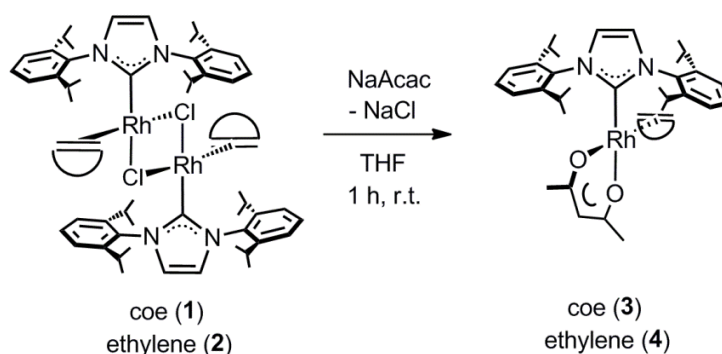
## Introduction

Coordinationally unsaturated organometallic species are fundamental cornerstones in transition metal-mediated catalytic cycles.<sup>1</sup> Despite recent success on isolation of such low-coordinate complexes,<sup>2,3</sup> their access and stabilization still remains an important challenge. These species may be relevant for the structural fine-tuning of the catalyst precursors provided that a control on the coordination properties of the metallic center could be exerted.<sup>4</sup> In this context, the advent of N-heterocyclic carbenes (NHCs)<sup>5</sup> as ligands for transition metal complexes has allowed an enhancement of both, catalytic activity<sup>6</sup> and stability of low-coordinate species.<sup>3</sup> Particularly for rhodium, the easy preparation of mononuclear complexes of type  $\text{RhCl}(\text{NHC})(\eta^4\text{-cod})$  ( $\text{cod} = 1,5\text{-cyclooctadiene}$ ) or  $\text{RhCl}(\text{NHC})(\text{CO})_2$ , from the dimer  $[\text{Rh}(\mu\text{-Cl})(\eta^4\text{-cod})]_2$ , has motivated their adoption as standard derivatives for the evaluation of stereoelectronic properties of any new NHC ligand,<sup>5</sup> although the development of the associated organometallic chemistry or catalytic applications has met limited success. In contrast, dinuclear monolefin complexes of type  $[\text{Rh}(\mu\text{-Cl})(\text{NHC})(\eta^2\text{-olefin})]_2$  have revealed as readily modifiable precursors for a rich variety of  $\text{Rh}^{\text{I}}$  and  $\text{Rh}^{\text{III}}$  organometallic complexes.<sup>7</sup> In view of this, we envisaged the use of these dimers to access the putative highly unsaturated  $[\text{Rh-NHC}]^+$  species stabilized by labile ligands as relevant species for the modulation of the electronic density at the rhodium center by selective coordination of the appropriate ligands.

## Results and Discussion

The first step in the “undressing” of  $[\text{Rh}(\mu\text{-Cl})(\text{NHC})(\eta^2\text{-olefin})]_2$  is the removal of the chlorido ligand. Unfortunately, reaction of  $[\text{Rh}(\mu\text{-Cl})(\text{IPr})(\eta^2\text{-olefin})]_2$  (olefin = coe (cyclooctene), **1**; ethylene, **2**) (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene) with silver or thallium

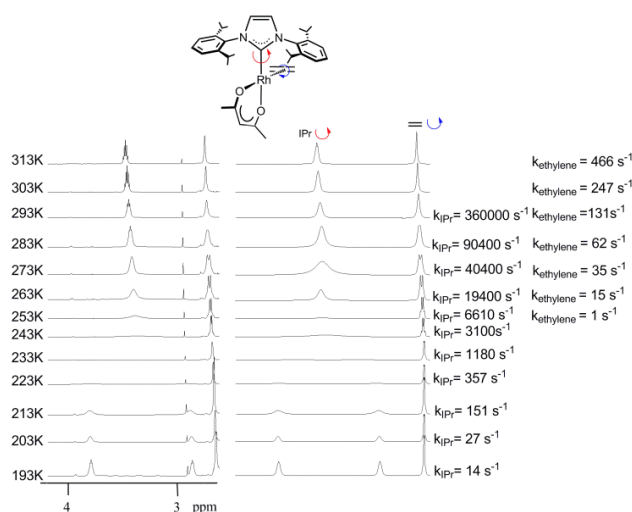
salts was unsuccessful. However, treatment of **1** and **2** with sodium acetylacetonate (acac) in THF at room temperature gave rise to monomeric square-planar derivatives Rh(acac)(IPr)( $\eta^2$ -olefin) (olefin = coe, **3**; ethylene **4**) which were isolated as yellow solids in 78 and 65 % molar yields, respectively (Scheme 1). Complexes **3** and **4** are interesting precursors featuring a Rh-NHC skeleton with two easily exchangeable ligands (acac and coe).<sup>8</sup>



**Scheme 1.** Synthesis of mononuclear Rh(acac)( $\eta^2$ -olefin)(IPr) complexes.

The  $^1\text{H}$  NMR spectra of **3** and **4** in  $\text{C}_6\text{D}_6$  showed the characteristic  $=\text{CH}$  proton of the acac ligand at  $\delta$  5.19 (**3**) and 5.09 (**4**) ppm. The  $\eta^2$ -olefin ligands were observed as broad signals high field shifted at 2.95 ppm for the coe derivative **3** and at 2.92 and 2.39 ppm for the ethylene counterpart **4**. The most interesting feature of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra is the presence of two doublets corresponding to the IPr (187.8 ppm,  $J_{\text{C-Rh}} = 59.6$  Hz, **3**; 186.1 ppm,  $J_{\text{C-Rh}} = 60.1$  Hz, **4**) and  $\eta^2$ -olefin (58.2 ppm,  $J_{\text{C-Rh}} = 16.0$  Hz, **3**; 42.5 ppm,  $J_{\text{C-Rh}} = 17.0$  Hz, **4**) ligands. The observation of a single resonance for the two olefinic carbon atoms reveals an out-of-plane coordination of the olefin ligands.<sup>9</sup> Complexes **3** and **4** showed a dynamic behavior as it was evidenced in their  $^1\text{H}$  VT-NMR spectra in  $\text{CD}_2\text{Cl}_2$  (Figure 1). At room temperature only one septet (CH) and two doublets ( $\text{CH}_3$ ) were observed for the four isopropyl groups of the IPr ligand, which split into two septets (CH) and four doublets ( $\text{CH}_3$ ) at low

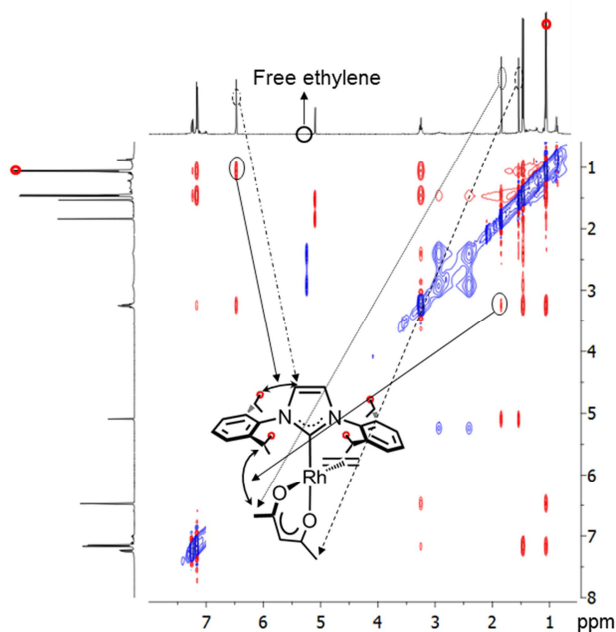
temperature. This fact could be ascribed to two factors: the existence of a mirror plane containing the acac ligand that bisects the imidazole ring, and a rotational process for the carbene ligand around the Rh-C<sub>IPr</sub> bond.<sup>10</sup> The activation parameters obtained from the corresponding Eyring analysis were  $\Delta H^\ddagger = 12.7 \pm 0.4 \text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta S^\ddagger = 1.4 \pm 0.8 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for **3**, and  $\Delta H^\ddagger = 10.4 \pm 0.3 \text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta S^\ddagger = 0.7 \pm 0.7 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for **4**. The lower value obtained for **4** is in accordance with the less sterically demanding ethylene ligand. These values are similar to that determined previously for related Rh<sup>I</sup>-IPr complexes.<sup>7g,10h</sup> Moreover, the coordinated ethylene in **4** undergoes internal rotation,<sup>11</sup> with activation parameters of  $\Delta H^\ddagger = 13.8 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta S^\ddagger = -1.5 \pm 1.3 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .



**Figure 1.** Variable-temperature  $^1\text{H}$  NMR spectra of Rh(acac)(IPr)( $\eta^2$ -ethylene) (**4**) in  $\text{CD}_2\text{Cl}_2$  showing the coalescence of the CH-isopropyl (IPr) and ethylene resonances: experimental (left) and calculated (right).

As expected, the methyl groups of the acac ligand in **3** and **4** are inequivalent which provides valuable stereochemical information on the complexes. A  $^1\text{H}$ - $^1\text{H}$  2D-NOESY spectrum of **4** in  $\text{C}_6\text{D}_6$  displays a correlation peak between the CH resonance of the IPr (3.25 ppm) and one of the

methyl group of the acac (1.84 ppm) indicating proximity of both fragments (Figure 2). More interestingly, the spectrum reveals that rotation of the isopropyl groups of IPr ligand is hindered. The imidazole =CH protons correlate with only one set of methyl-IPr signals (1.06 ppm), the “upper” part, whereas the methyl group of the acac ligand correlates with the other doublet (1.46 ppm) corresponding to the methyl-IPr pointing to the rest of the ligands. Exchange crosspeaks between the ethylene signals (2.92 and 2.39 ppm) were observed which is in accordance with the dynamic behavior described above. In addition, exchange correlation peaks between coordinated and free ethylene, observed at 5.24 ppm, were also detected which reveals the labile character of the ethylene ligand.



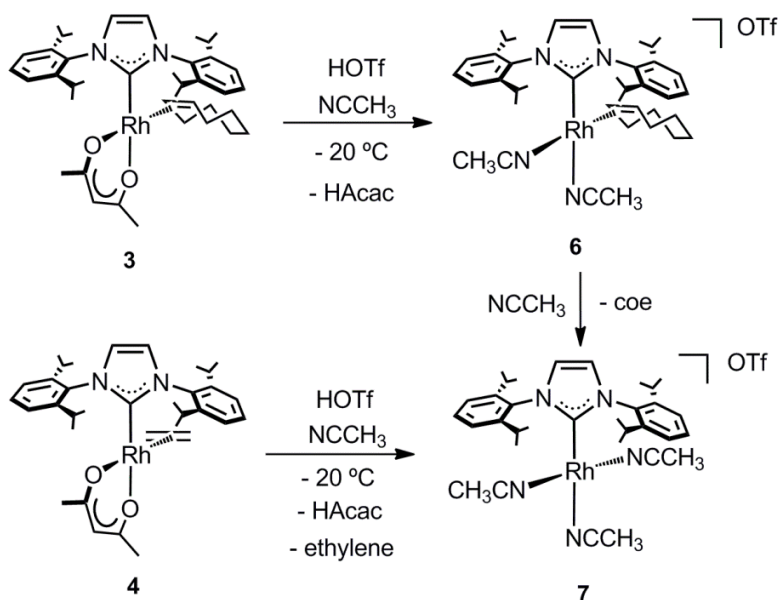
**Figure 2.**  $^1\text{H}$ - $^1\text{H}$  2D-NOESY spectrum of **4** in  $\text{C}_6\text{D}_6$  at room temperature.

The next step to access the bare  $[\text{Rh-NHC}]^+$  fragment consisted in the removal of the chelate acac ligand that could be easily achieved by protonation. Thus, treatment of **3** with HOTf (OTf = trifluoromethanesulfonate) at  $-20\text{ }^\circ\text{C}$  gave rise to the formation of  $\text{Rh}(\text{OTf})(\text{IPr})(\eta^2\text{-coe})$  (**5**) as a

very unstable pale yellow solid. Similar procedure starting from **4** gave a mixture of unidentified products probably by competitive formation of Rh-ethyl species.<sup>12</sup> The presence of both IPr and  $\eta^2$ -coe ligands in **5** was corroborated by NMR spectroscopy at low temperature. The  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  showed a resonance at 2.83 ppm ascribed to the =CH protons of the coe ligand, whereas two doublets for IPr (171.7 ppm,  $J_{\text{C-Rh}} = 71.7$  Hz), and the  $\eta^2$ -olefin (57.1 ppm,  $J_{\text{C-Rh}} = 19.0$  Hz) were observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. The triflate ligand may occupy the two available vacant sites by bidentate chelate or bridging fashion.<sup>13</sup> However, the stretching bands for the  $\text{SO}_3$  group in the IR spectrum at 1310 and 1181  $\text{cm}^{-1}$  do not clarify the coordination mode.<sup>13</sup> More important are the two down-field shifted broad signals observed in the  $^{19}\text{F}$  NMR spectrum at -76.4 and -77.6 ppm that might suggest the interaction of the fluoride atoms with the rhodium centre or their participation in some hydrogen bond. DFT calculations for three different  $\eta^2$ -OTf coordination modes showed that  $\kappa^2\text{-O,O'}$  is 7.6 and 8.8  $\text{kcal}\cdot\text{mol}^{-1}$  more stable than  $\kappa\text{-O},\kappa\text{-F}$  (See Figure S1 in Supporting Information). A minimum containing a  $\eta^1$ -OTf ligand could not be found. In spite of the theoretical findings in gas phase, the existence of dynamic processes or the formation of polynuclear aggregates in solution should not be excluded.

The high unstability of **5** makes it an impractical organometallic precursor. However, stabilization of **5** at low temperature in the presence of  $\text{CH}_3\text{CN}$  gave rise to the cationic derivative  $[\text{Rh}(\text{IPr})(\eta^2\text{-coe})(\text{NCCH}_3)_2]\text{OTf}$  (**6**), which was isolated as a white solid in 75 % yield (Scheme 2). The cationic fragment  $[\text{Rh-IPr}]^+$  in **6** is stabilized with two kind of labile ligands which could potentially favor selective further modifications.<sup>14</sup> In fact, the coe ligand was released when an acetonitrile solution of **6** was warmed to room temperature to give  $[\text{Rh}(\text{IPr})(\text{NCCH}_3)_3]\text{OTf}$  (**7**),<sup>15</sup> which was isolated as a white solid in 76% yield. When starting from the  $\eta^2$ -ethylene derivative **4**, it was not possible to isolate an intermediate similar to **6**, as **7**

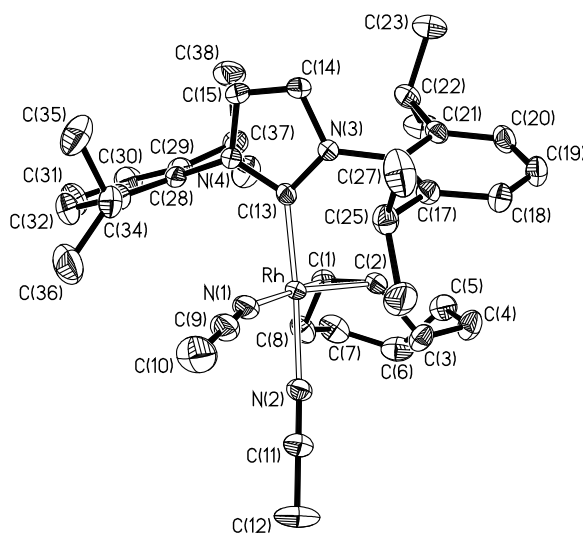
was immediately formed after the addition of triflic acid to an acetonitrile solution of **4** even at -20 °C (Scheme 2).



**Scheme 2.** Access to the Rh-IPr<sup>+</sup> fragment stabilized by labile ligands.

Complex **6** has been characterized by elemental analysis, IR and NMR spectroscopies, and it was further characterized by an X-ray diffraction analysis. Figure 3 displays a view of the cation of **6**. The complex has a distorted square-planar structure with IPr and coe (Ct\*-Rh-C(13) 94.62(6)°) and acetonitrile ligands (N(1)-Rh-N(2) 82.96(6)°) in *cis* relative disposition (Ct\* represents the midpoint of the olefinic C(1)-C(2) double bond); the different steric requirements of the coordinated ligands easily justify the observed distortions from the *cis*-ideal 90° values. The Rh-carbene separation (1.9980(16) Å) falls within the shortest reported for other rhodium-NHC single-bond distances.<sup>5c</sup> (comentar distancias Rh-N efecto trans y estérico del NHC) The carbon-carbon double bond of the η<sup>2</sup>-coe ligand (C(1)-C(2) 1.390(2) Å) is also relatively short in accordance with a diminished retrodonation from a cationic Rh<sup>I</sup> metal center. The imidazole ring is statistically planar and is arranged almost perpendicular to the metal coordination plane,

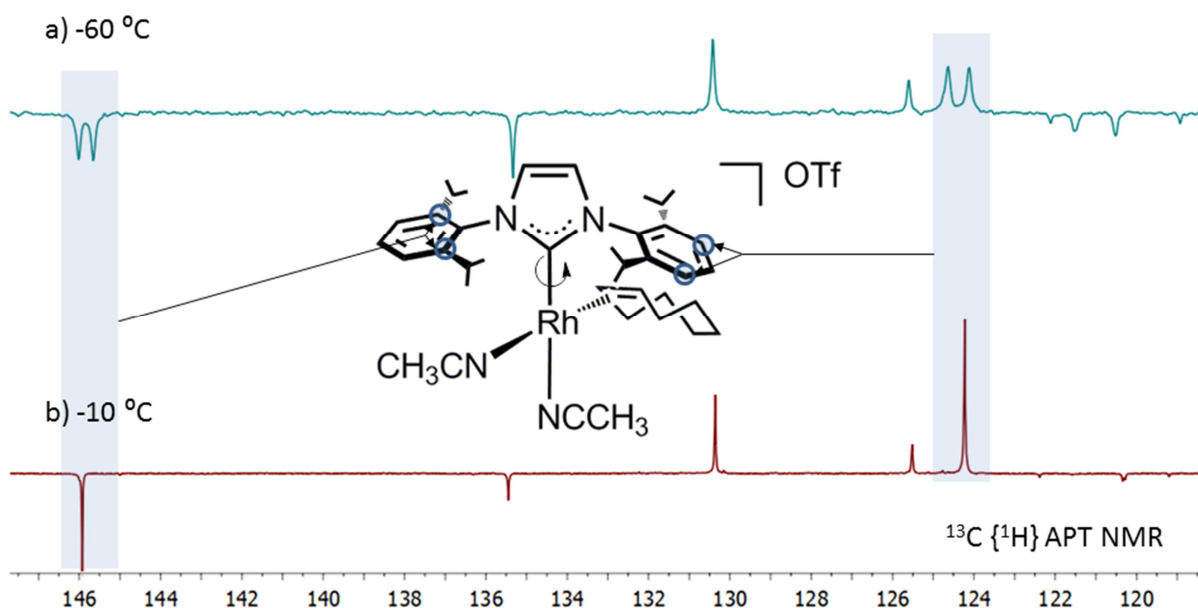
making a dihedral angle of 79.05(5)°. The tilt dihedral angles of the phenyl substituents respect to the imidazole plane are slightly different (78.91 and 86.19(7)°), most probably as a consequence of the more voluminous nature of the coe vs. acetonitrile. In spite of this, a *cis* disposition with regard to the bulky IPr is observed, probably due to electronic factors. It is rather surprising that the stronger  $\pi$ -acceptor ligand, coe in this case, does not coordinate *trans* to a powerful electron releasing ligand such as IPr. A rational explanation may arise as follows: the  $\pi$ -acidity of NHCs has revealed to be non negligible,<sup>16</sup> thus the greater  $\pi$ -acceptor ligand might coordinate in *cis* disposition to the NHC in order to prevent competitive interaction with occupied metal orbitals amenable to retrodonation.<sup>17</sup>



**Figure 3.** Molecular diagram for the cation of **6**. Selected bond lengths (Å) and angles (°): Rh-N(1) 2.0725(16), Rh-N(2) 2.0607(15), Rh-C(1) 2.1460(18), Rh-C(2) 2.1272(17), Rh-C(13) 1.9980(16), C(1)-C(2) 1.390(2); N(1)-Rh-N(2) 82.96(6), N(1)-Rh-Ct\* 172.13(6), N(1)-Rh-C(13) 89.47(6), N(2)-Rh-Ct\* 92.89(6), N(2)-Rh-C(13) 172.43(6), Ct\*-Rh-C(13) 94.62(6).



The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  at  $-20\text{ }^\circ\text{C}$  of **6** are consistent with the structure shown in figure **3**. The  $=\text{CH}$  protons of the  $\eta^2$ -olefin resonates at  $\delta$  3.22 ppm whereas two singlets are observed at 2.37 and 2.11 ppm for the inequivalent acetonitrile molecules. Similarly to **3** and **4**, the IPr ligand of **6** rotates around the  $\text{R-C}_{\text{IPr}}$  bond. In this case it was not possible to calculate activation parameters from CH isopropyl-IPr signals due to accidental isochronism, thus it was taken advantage of the fluxionality of  $\text{CH}_{\text{meta}}$  protons of the 2,6-diisopropylphenyl substituents. A value of  $\Delta H^\ddagger = 12.7 \pm 0.3\text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta S^\ddagger = 1.4 \pm 0.9\text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  was found, very similar to that found in  $\eta^2$ -coe complex **3**. This rotational process can also be nicely observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra recorded at  $-60$  and  $-10\text{ }^\circ\text{C}$  (Figure 4). The doublets assigned to the carbon atoms directly bonded to rhodium did not change significantly with temperature (IPr, 175.1 ppm,  $J_{\text{C-Rh}} = 55.3\text{ Hz}$ ; coe, 70.1 ppm,  $J_{\text{C-Rh}} = 14.3\text{ Hz}$  at  $-60\text{ }^\circ\text{C}$ ). However, both resonances corresponding to the quaternary carbons attached to the isopropyl substituents and the  $\text{CH}_{\text{meta}}$  carbon atoms, split into a pair of signals at  $-60\text{ }^\circ\text{C}$  due to the stopping of the rotational motion. The frozen structure presents a mirror plane that bisects both the imidazole ring and coe, and contains both acetonitrile ligands, similarly to that observed in the solid state where the imidazole has been found nearly perpendicular to the metal coordination plane.



**Figure 4.**  $^{13}\text{C}\{^1\text{H}\}$ -APT NMR spectra of **6** at  $-60\text{ }^{\circ}\text{C}$  (a) and  $-10\text{ }^{\circ}\text{C}$  (b).

The structure of  $[\text{Rh}(\text{IPr})(\text{NCCH}_3)_3]\text{OTf}$  (**7**) was corroborated by elemental analysis, and IR and NMR spectroscopies. The presence of acetonitrile ligands was confirmed by the  $\text{C}\equiv\text{N}$  stretching bands in IR spectrum at  $2331$  and  $2297\text{ cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra in  $\text{CD}_3\text{CN}$  showed the expected set of resonances for the IPr ligand, in full agreement with the  $\text{C}_{2v}$  symmetry, and free acetonitrile due to exchange with  $\text{CD}_3\text{CN}$ . In addition, the  $^{19}\text{F}$  NMR spectrum showed a singlet at  $-78.8\text{ ppm}$  that supports the cationic formulation of **7**.<sup>13</sup> Complex **7** was isolated as a white solid, which is not stable in solvents other than acetonitrile. It is well known the stabilization of highly reactive metal-fragments by acetonitrile coordination.<sup>15c,18</sup> Thus, complex **7** can be considered as the final stage of the process to access to putative bare  $[\text{Rh}-\text{NHC}]^+$  fragment, which is further supported by the presence of labile acetonitrile ligands.

## Concluding Remarks

The dinuclear olefin species  $[\text{Rh}(\mu\text{-Cl})(\eta^2\text{-olefin})(\text{IPr})]_2$  are useful precursors for the access to labile complexes. First, metathesis reaction with sodium acetylacetonate gives the square planar complexes  $\text{Rh}(\text{acac})(\eta^2\text{-olefin})(\text{IPr})$ . Then, the protonation of the  $\text{acac}^-$  ligand with triflic acid resulted in the formation of the putative highly unsaturated  $[\text{Rh-IPr}]^+$  fragment that has been stabilized at low temperature by coordinated triflate, *coe* or acetonitrile ligands. In particular, the labile cationic  $[\text{Rh}(\text{IPr})(\text{NCCH}_3)_3]^+$  species can be envisaged as a potential catalyst for organic transformations as well as a valuable precursor for the preparation of new cationic Rh-NHC square-planar derivatives. Further work on the potential applications both in synthesis and catalysis is currently being developed in our group.

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Note: the authors declare no competing financial interest

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**Supporting Information Available.** X-ray crystallographic information files containing full details of the structural analysis of complex **6** (CIF format). Figure S1 and cartesian coordinate

for theoretical calculated **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The dinuclear complexes **1**<sup>7b</sup> and **2**<sup>7g</sup> were prepared as previously described in the literature. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (<sup>1</sup>H, <sup>13</sup>C) or external H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) or CFC<sub>3</sub> (<sup>19</sup>F). Coupling constants, *J*, are given in hertz. Spectral assignments were achieved by combination of <sup>1</sup>H-<sup>1</sup>H COSY, <sup>13</sup>C APT, and <sup>1</sup>H-<sup>13</sup>C HSQC/HMBC experiments. C, H, and N analysis were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer, using a Universal ATR Sampling Accessory (neat samples).

**Preparation of Rh(acac)(IPr)( $\eta^2$ -coe) (**3**).** An orange solution of **1** (660 mg, 0.518 mmol) in THF (20 mL) was treated with sodium acetylacetonate (139 mg, 1.14 mmol) and stirred at room temperature for 1 h. After filtration through celite, the THF was removed in vacuo, the residue redissolved in toluene (15 mL) and the mixture once again filtered and evaporated to dryness. Addition of *n*-hexane at -40 °C caused the precipitation of a yellow solid which was washed with cold *n*-hexane (3 x 3 mL) at low temperature and dried in vacuo. Yield: 564 mg (78%). Anal. Calcd. for C<sub>40</sub>H<sub>58</sub>N<sub>2</sub>O<sub>2</sub>Rh: C, 68.48; H, 8.28; N, 3.99. Found: C, 68.26; H, 8.12; N, 4.06. IR (cm<sup>-1</sup>):  $\nu$ (C=O) 1583 (s) and 1514 (s). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.30 (t, *J*<sub>H-H</sub> = 7.6, 2H, H<sub>p-Ph</sub>), 7.21 (d, *J*<sub>H-H</sub> = 7.6, 4H, H<sub>m-Ph</sub>), 6.50 (s, 2H, =CHN), 5.19 (s, 1H, CH<sub>acac</sub>), 3.13 (br, 4H,

$\underline{\text{CHMe}}_{\text{IPr}}$ , 2.95 (m, 2H,  $=\text{CH}_{\text{coe}}$ ), 2.16, 1.82, 1.60, and 1.36 (all m, 12H,  $\text{CH}_{2\text{-coe}}$ ), 1.93 and 1.56 (both s, 6H,  $\text{Me}_{\text{acac}}$ ), 1.42 and 1.06 (both d,  $J_{\text{H-H}} = 6.9$ , 24H,  $\underline{\text{CHMe}}_{\text{IPr}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (125.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  187.8 (d,  $J_{\text{C-Rh}} = 59.6$ , Rh- $\text{C}_{\text{IPr}}$ ), 185.0 and 182.6 (both s, CO), 146.8 (s,  $\text{C}_{\text{q-IPr}}$ ), 137.3 (s,  $\text{C}_{\text{qN}}$ ), 129.5 (s,  $\text{CH}_{\text{m-Ph}}$ ), 124.0 (s,  $=\text{CHN}$ ), 123.8 (s,  $\text{CH}_{\text{p-Ph}}$ ), 98.5 (s,  $\text{CH}_{\text{acac}}$ ), 58.2 (d,  $J_{\text{C-Rh}} = 16.0$ ,  $\text{CH}_{\text{coe}}$ ), 30.4, 28.2, and 27.1 (all s,  $\text{CH}_{2\text{-coe}}$ ), 28.5 (s,  $\underline{\text{CHMe}}_{\text{IPr}}$ ), 27.8 and 27.7 (both s,  $\text{Me}_{\text{acac}}$ ), 26.4 and 23.0 (both s,  $\underline{\text{CHMe}}_{\text{IPr}}$ ). Mp (150 °C, decomposition).

**Preparation of  $\text{Rh}(\text{acac})(\text{IPr})(\eta^2\text{-CH}_2=\text{CH}_2)$  (4).** The complex was prepared from **2** (393 mg, 0.308 mmol) and sodium acetylacetonate (95 mg, 0.78 mmol) following the procedure described for **3**. Yield: 285 mg (65%). Anal. Calcd. for  $\text{C}_{34}\text{H}_{48}\text{N}_2\text{O}_2\text{Rh}$ : C, 65.92; H, 7.76; N, 4.52. Found: C, 66.26; H, 7.34; N, 4.41. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{O})$  1576 (s) and 1512 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.24 (t,  $J_{\text{H-H}} = 7.6$ , 2H,  $\text{H}_{\text{p-Ph}}$ ), 7.15 (d,  $J_{\text{H-H}} = 7.6$ , 4H,  $\text{H}_{\text{m-Ph}}$ ), 6.48 (s, 2H,  $=\text{CHN}$ ), 5.09 (s, 1H,  $\text{H}_{\text{acac}}$ ), 3.25 (sept, 4H,  $\underline{\text{CHMe}}_{\text{IPr}}$ ), 2.92 and 2.39 (br, 4H,  $\text{CH}_2=\text{CH}_2$ ), 1.84 and 1.54 (both s, 6H,  $\text{Me}_{\text{acac}}$ ), 1.46 and 1.06 (both d,  $J_{\text{H-H}} = 6.8$ , 24H,  $\underline{\text{CHMe}}_{\text{IPr}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (125.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  186.1 (d,  $J_{\text{C-Rh}} = 60.1$ , Rh- $\text{C}_{\text{IPr}}$ ), 185.7 and 183.3 (both s, CO), 146.5 (s,  $\text{C}_{\text{q-IPr}}$ ), 137.2 (s,  $\text{C}_{\text{qN}}$ ), 129.4 (s,  $\text{CH}_{\text{m-Ph}}$ ), 124.0 (s,  $=\text{CHN}$ ), 123.9 (s,  $\text{CH}_{\text{p-Ph}}$ ), 98.8 (s,  $\text{CH}_{\text{acac}}$ ), 42.5 (d,  $J_{\text{C-Rh}} = 17.0$ ,  $\text{CH}_2=\text{CH}_2$ ), 28.6 (s,  $\underline{\text{CHMe}}_{\text{IPr}}$ ), 27.5 and 27.3 (both s,  $\text{Me}_{\text{acac}}$ ), 26.0 and 23.2 (both s,  $\underline{\text{CHMe}}_{\text{IPr}}$ ). Mp (150 °C, decomposition).

**Preparation of  $\text{Rh}(\text{OTf})(\text{IPr})(\eta^2\text{-coe})$  (5).** A yellow solution of **3** (100 mg, 0.142 mmol) in diethyl ether (5 mL) at -20 °C was treated with triflic acid (14  $\mu\text{L}$ , 0.15 mmol). After the solution was stirred for 15 min, the solvent was evaporated to dryness at low temperature. Subsequent addition of *n*-hexane at -20 °C caused the precipitation of a pale yellow solid which was washed with *n*-hexane (3 x 3 mL) and dried in vacuo maintaining the temperature under -20 °C. Yield 83 mg (77%). IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{a}}(\text{SO}_3)$  1310 (s);  $\nu_{\text{s}}(\text{CF}_3)$  1216 (m);  $\nu_{\text{a}}(\text{CF}_3)$  1181 (s);  $\nu_{\text{s}}(\text{SO}_3)$  1008 (s);

$\delta_a(\text{SO}_3)$  628 (s). Satisfactory elemental analysis could not be obtained due to thermal instability of **5**.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  7.28 (t,  $J_{\text{H-H}} = 7.0$ , 2H,  $\text{H}_{\text{p-Ph}}$ ), 7.19 (d,  $J_{\text{H-H}} = 7.0$ , 4H,  $\text{H}_{\text{m-Ph}}$ ), 6.40 (s, 2H,  $=\text{CHN}$ ), 2.92 (br, 4H,  $\text{CHMe}_{\text{IPr}}$ ), 2.83 (m, 2H,  $=\text{CH}_{\text{coe}}$ ), 2.1-0.8 (m, 12H,  $\text{CH}_{2\text{-coe}}$ ), 1.52 and 0.96 (both d,  $J_{\text{H-H}} = 6.2$ , 24H,  $\text{CHMe}_{\text{IPr}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (75.1 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K): 171.7 (d,  $J_{\text{C-Rh}} = 71.7$ , Rh-C<sub>IPr</sub>), 146.2 (s, C<sub>q-IPr</sub>), 135.6 (s, C<sub>qN</sub>), 130.0 (s, CH<sub>m-Ph</sub>), 124.6 (s,  $=\text{CHN}$ ), 123.9 (s, CH<sub>p-Ph</sub>), 119.5 (q,  $J_{\text{C-F}} = 320.1$ , CF<sub>3</sub>), 57.1 (d,  $J_{\text{C-Rh}} = 19.0$ ,  $=\text{CH}_{\text{coe}}$ ), 29.1, 28.1, and 26.4 (all s,  $\text{CH}_{2\text{-coe}}$ ), 28.9 (s,  $\text{CHMe}_{\text{IPr}}$ ), 25.8 and 22.4 (both s,  $\text{CHMe}_{\text{IPr}}$ ).  $^{19}\text{F}$  NMR (282.3 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  -76.4 and -77.6 (both br)

**Preparation of  $[\text{Rh}(\text{IPr})(\eta^2\text{-coe})(\text{CH}_3\text{CN})_2]\text{OTf}$  (**6**).** A yellow solution of **3** (120 mg, 0.170 mmol) in diethyl ether (5 mL) was treated with acetonitrile (0.5 mL) and HOTf (19  $\mu\text{L}$ , 0.21 mmol) at  $-20^\circ\text{C}$  to give immediately a colorless solution. After the solution was stirred for 15 min, the solvent was evaporated to ca. 0.5 mL at low temperature. Subsequent addition of diethyl ether at  $-20^\circ\text{C}$  caused the precipitation of a white solid which was washed with diethyl ether (3 x 3 mL) and dried in vacuo maintaining the temperature under  $-20^\circ\text{C}$ . Yield: 275 mg (75%). Anal. Calcd. for  $\text{C}_{40}\text{H}_{56}\text{N}_4\text{SF}_3\text{O}_3\text{Rh}$ : C, 57.70; H, 6.73; N, 6.73; S, 3.85. Found: C, 57.42; H, 6.27; N, 6.54; S, 3.74. IR ( $\text{cm}^{-1}$ ):  $\nu$  ( $\text{CH}_3\text{CN}$ ) 2330 and 2302 (w);  $\nu_a(\text{SO}_3)$  1259 (s);  $\nu_s(\text{CF}_3)$  1223 (m);  $\nu_a(\text{CF}_3)$  1152 (s);  $\nu_s(\text{SO}_3)$  1029 (s);  $\delta_a(\text{SO}_3)$  635 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 253 K):  $\delta$  7.61 (t,  $J_{\text{H-H}} = 6.8$ , 2H,  $\text{H}_{\text{p-Ph}}$ ), 7.43 (d,  $J_{\text{H-H}} = 6.8$ , 4H,  $\text{H}_{\text{m-Ph}}$ ), 7.10 (s, 2H,  $=\text{CHN}$ ), 3.22 (m, 2H,  $=\text{CH}_{\text{coe}}$ ), 2.98 (br, 4H,  $\text{CHMe}_{\text{IPr}}$ ), 2.37 and 2.11 (both s, 6H,  $\text{CH}_3\text{CN}$ ), 1.5-1.0 (m, 12H,  $\text{CH}_{2\text{-coe}}$ ), 1.42 and 1.04 (both d,  $J_{\text{H-H}} = 6.8$ , 24H,  $\text{CHMe}_{\text{IPr}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (100.4 MHz,  $\text{CD}_2\text{Cl}_2$ , 213 K):  $\delta$  175.1 (d,  $J_{\text{C-Rh}} = 55.3$ , Rh-C<sub>IPr</sub>), 145.5 and 145.1 (both s, C<sub>q-IPr</sub>), 134.8 (s, C<sub>qN</sub>), 129.9 (s, CH<sub>p-Ph</sub>), 125.1 (s,  $=\text{CHN}$ ), 124.1 and 123.6 (both s, CH<sub>m-Ph</sub>), 121.0 and 120.0 (both s,  $\text{CH}_3\text{CN}$ ), 129.8 (q,  $J_{\text{C-F}} = 320.2$ , CF<sub>3</sub>), 70.1 (d,  $J_{\text{C-Rh}} = 14.3$ ,  $\text{CH}_{\text{coe}}$ ), 29.8, 29.6, and 26.1 (all s,  $\text{CH}_{2\text{-coe}}$ ),

28.4 and 28.3 (both s,  $\underline{\text{CHMe}}_{\text{IPr}}$ ), 26.4, 26.3, 22.8, and 21.6 (all s,  $\text{CHMe}_{\text{IPr}}$ ), 3.67 (s,  $\underline{\text{CH}_3\text{CN}}$ ).  $^{19}\text{F}$  NMR (282.3 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  -78.9 (s). Mp (140 °C, decomposition).

**Preparation of  $[\text{Rh}(\text{IPr})(\text{CH}_3\text{CN})_3]\text{OTf}$  (7).** This complex was prepared from **4** (120 mg, 0.194 mmol), acetonitrile (0.5 mL), and HOTf (19  $\mu\text{L}$ , 0.21 mmol) following the procedure described above for **6** and isolated as a white solid. Yield: 112 mg (76%). Anal. Calcd. for  $\text{C}_{34}\text{H}_{45}\text{N}_5\text{SF}_3\text{O}_3\text{Rh}$ : C, 52.69; H, 5.90; N, 9.18; S, 4.19. Found: C, 52.35; H, 5.75; N, 8.92; S, 3.78. IR ( $\text{cm}^{-1}$ ):  $\nu$  ( $\text{CH}_3\text{CN}$ ) 2331 and 2297 (w);  $\nu_{\text{a}}(\text{SO}_3)$  1250 (s);  $\nu_{\text{s}}(\text{CF}_3)$  1222 (m);  $\nu_{\text{a}}(\text{CF}_3)$  1153 (s);  $\nu_{\text{s}}(\text{SO}_3)$  1028 (s);  $\delta_{\text{a}}(\text{SO}_3)$  636 (s).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ , 298 K):  $\delta$  7.62 (t,  $J_{\text{H-H}} = 7.7$ , 2H,  $\text{H}_{\text{p-Ph}}$ ), 7.47 (d,  $J_{\text{H-H}} = 7.7$ , 4H,  $\text{H}_{\text{m-Ph}}$ ), 7.33 (s, 2H,  $=\text{CHN}$ ), 2.72 (sept,  $J_{\text{H-H}} = 6.9$ , 4H,  $\underline{\text{CHMe}}_{\text{IPr}}$ ), 1.36 and 1.14 (both d,  $J_{\text{H-H}} = 6.9$ , 24H,  $\text{CHMe}_{\text{IPr}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ -APT NMR (75.1 MHz,  $\text{CD}_3\text{CN}$ , 298 K):  $\delta$  182.8 (d,  $J_{\text{C-Rh}} = 53.4$ , Rh- $\text{C}_{\text{IPr}}$ ), 147.2 (s,  $\text{C}_{\text{q-IPr}}$ ), 137.5 (s,  $\text{C}_{\text{qN}}$ ), 130.8 (s,  $\text{CH}_{\text{m-Ph}}$ ), 125.6 (s,  $=\text{CHN}$ ), 124.8 (s,  $\text{CH}_{\text{p-Ph}}$ ), 120.4 (q,  $J_{\text{C-F}} = 320.2$ ,  $\text{CF}_3$ ), 29.4 (s,  $\underline{\text{CHMe}}_{\text{IPr}}$ ), 27.5, 26.0, and 22.8 (all s,  $\text{CHMe}_{\text{IPr}}$ ).  $^{19}\text{F}$  NMR (282.3 MHz,  $\text{CD}_3\text{CN}$ , 298 K):  $\delta$  -78.8 (s). Mp (160 °C, decomposition).

**X-ray Structural Determination of  $[\text{Rh}(\text{IPr})(\eta^2\text{-coe})(\text{CH}_3\text{CN})_2]\text{OTf}$  (6).** A prismatic crystal suitable for X-ray diffraction analysis was obtained by slow diffusion of diethylether into a concentrated dichloromethane solution of **6** at 253 K. Intensity data were collected at low temperature (100(2) K) with graphite-monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å), using narrow  $\phi$  or  $\omega$  rotations ( $0.3^\circ$ ) on a Bruker DUO APEX2 area detector diffractometer. Cell parameters were refined from the observed setting angles and detector positions of strong reflections (9909 refl.,  $2\theta < 60.23^\circ$ ). Intensities were integrated and corrected for absorption effects using SAINT+,<sup>19</sup> and SADABS<sup>20</sup> programs, included in APEX2 package. The structure was solved by Patterson methods and completed by successive difference Fourier syntheses

(SHELXS-97).<sup>21</sup> Refinement was carried out, by full-matrix least-squares on  $F^2$ , including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen non-disordered atoms (SHELXL-97).<sup>22</sup> The triflate anion was observed disordered; two CF<sub>3</sub>SO<sub>3</sub> units with complementary occupancy factors, were included in the refinement. All hydrogen atoms (except those of the coordinated olefin) were included in calculated positions and refined with displacement and positional riding parameters. At this point, three high residuals, far from the metal complex, showed the existence of some disordered solvent in the crystal structure. Several attempts to model some kind of solvent disorder were carried out but geometrical and crystallographic parameters coming out from these calculations were not reasonable. Eventually an analysis was carried out with SQUEEZE program<sup>23</sup> giving rise to a solvent/void volume of 120.3 Å<sup>3</sup> and an estimated electron density of 43 e<sup>-</sup>. These values were interpreted assuming the presence of a disordered CH<sub>2</sub>Cl<sub>2</sub> solvent molecule and the structure factors accordingly modified.<sup>23</sup> After proper refinement convergence, the highest residuals (<1.03 e/Å<sup>3</sup>) were close to the metal atom, or in the region of the disordered triflate anion, and have no chemical sense.

**Crystal data for 6:** C<sub>40</sub>H<sub>56</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>RhS 0.5(CH<sub>2</sub>Cl<sub>2</sub>),  $M = 875.32$ ; colorless prism,  $0.137 \times 0.174 \times 0.184$  mm<sup>3</sup>; triclinic,  $P-1$ ;  $a = 10.6930(8)$ ,  $b = 13.4285(10)$ ,  $c = 17.2274(13)$  Å,  $\alpha = 68.9360(10)$ ,  $\beta = 81.9510(10)$ ,  $\gamma = 67.8920(10)^\circ$ ;  $Z = 2$ ;  $V = 2138.7(3)$  Å<sup>3</sup>;  $D_c = 1.359$  g/cm<sup>3</sup>;  $\mu = 0.564$  mm<sup>-1</sup>, min. and max. absorp. correct. fact. 0.822 and 0.940;  $2\theta_{\max} = 61.04^\circ$ ; 25480 collected reflections, 11898 unique [ $R_{\text{int}} = 0.0248$ ]; number of data/restraints/parameters 11898/0/523; final  $GoF$  1.069;  $R1 = 0.0346$  [10441 reflections,  $I > 2\sigma(I)$ ];  $wR2 = 0.0915$  for all data.

**Determination of rotational barriers.** Full line-shape analysis of the dynamic <sup>1</sup>H NMR spectra of **3**, **4** and **6** were carried out using the program gNMR (Cherwell Scientific Publishing



Limited). The transverse relaxation time,  $T_2$ , was estimated at the lowest temperature. Activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were obtained by linear least-squares fit of the Eyring plot. Errors were computed by published methods.<sup>24</sup>

**DFT calculations.** All calculations were performed with the Gaussian09 package<sup>25</sup> at the B3LYP level.<sup>26</sup> Rhodium was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set (SDD keyword in Gaussian 09).<sup>27</sup> The 6-31G(d) basis set was used for all the other atoms (C, N, O, H, S, F).<sup>28</sup> Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the stationary points as minima on the potential energy surface.

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